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Adsorption and desorption kinetics of D_2 and H_2 on metallic reconstructed surfaces: a Monte Carlo simulation

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Abstract. We study dissociative adsorption kinetics of H_2 and D_2 on W (001).

The dissociative (associative) adsorption (desorption) kinetics of H_2 and D_2 on W (001) based on a simple model developed in [1] is studied. The dependence of the sticking coefficient $S(\theta)$, the desorption rate constant $K_d(\theta)$ and the Arrhenius parameters with the coverage have been analysed. The effect on the kinetics of the translational partition function of the activated complex, and the interaction of this with its neighbourhood, are also considered.

The W (001) face reconstructs in such a way that three relative positions of W atoms are found on the surface: (i) W atoms are closer than in the original lattice, (ii) the relative distance is the same as in the original lattice, and (iii) they are further apart than in the original lattice. We assume that in (iii) there is an additional adsorptive energy for H or D atoms (the heterogeneity hypothesis). The basic equations used in the simulation to analyse the kinetic parameters are [2]

$$\frac{S(\theta)}{S(0)} = p_{\mathrm{oo}} \sum_i \frac{F_{\mathrm{H^*D^*},i}}{F_{\mathrm{H^*D^*,o}}} P_{\mathrm{oo},i} \exp(-\varepsilon_i^*/RT)$$

$$\frac{K_d(\theta)}{K_d^{\mathrm{o}}} = \sum_i \frac{F_{\mathrm{H^*D^*},i}}{F_{\mathrm{H^*D^*,o}}} P_{\mathrm{HD},i} \exp[-(\varepsilon_i^* - \varepsilon_i) RT]$$

where p_{oo} is the probability of finding two empty nearest-neighbour sites, and $P_{\mathrm{oo},i}$ that for a pair of empty sites having an environment 'i'. The terms $F_{\mathrm{H^*D^*},i}$ and $F_{\mathrm{H^*D^*,o}}$ are the translational partition functions of the activated complex for neighbourhood 'i' and zero coverage, respectively. ε_i^* is the interaction of H^*D^* with the neighbourhood. $P_{\mathrm{HD},i}$ is the probability that two nearest-neighbour sites with H and D have a neighbourhood 'i'. ε_i denotes the lateral interactions of HD with the neighbourhood.

The Hamiltonian for this model can be written as

$$H = J \sum_{i\mathrm{NN}j} S_i S_j + \sum_{i \neq j} \varepsilon_{ij} n_i n_j + \lambda \sum_i n_i (S_{i+1} - S_i) + \sum_i E_i^{\mathrm{s}} n_i$$

where $J \sum S_i S_j$ is the W–W interaction term, S_i is the spin variable (+1 up, −1 down), $\sum \varepsilon_{ij} n_i n_j$ is the H–H, D–D and H–D NN and NNN interaction term, n_i is the occupation

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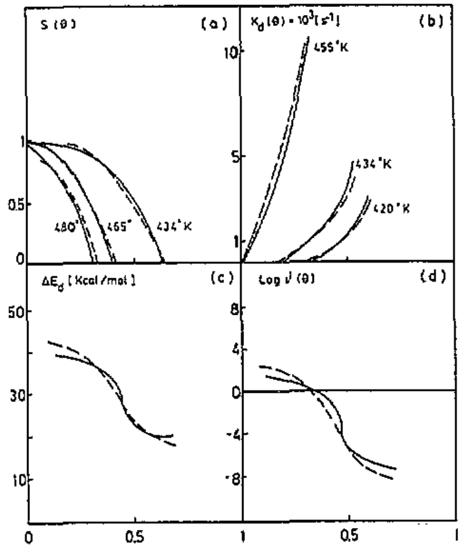

Figure 1. (*a*) Variation of the sticking probability with H + D coverage where the partial coverages of H and D are the same. Full curves: experimental results (the fitting curve of experimental result of [3]); broken curves: results of MC simulation. The values of energetic parameters are: $\lambda_H = 3\,\mathrm{kcal\,mol^{-1}}$, $\lambda_D = 2.4\,\mathrm{kcal\,mol^{-1}}$, $E_{H,D} = 3\,\mathrm{kcal\,mol^{-1}}$; $\varepsilon_{1HH} = \varepsilon_{1HD} = \varepsilon_{1DD} = -0.5\,\mathrm{kcal\,mol^{-1}}$; $\varepsilon_{2HH} = \varepsilon_{2HD} = \varepsilon_{2DD} = +0.5\,\mathrm{kcal\,mol^{-1}}$; $\varepsilon^* = -0.2\,\mathrm{kcal\,mol^{-1}}$. The same parameters are used throughout. (*b*) Variation of the desorption rate constant of HD as a function of H + D coverage. (*c*) Variation of the activation energy for desorption with coverage. $T = 434$ K. (*d*) Variation of the desorption pre-exponential factor $\nu(\theta)$ as function of H + D coverage. $T = 434$ K.

number for H or D, the third term represents the W–H or W–D interaction, and λ is in general different for H or D. The last term takes into account the effect of heterogeneity.

Simulated (broken curves) and experimental results (full curves) are shown in figure 1. The experimental results of [3] have been reproduced, confirming that the isotopic effects are negligible and the kinetics of H_2 and D_2 are similar.

To reproduce the experimental data, the following conditions must be satisfied in our model. (i) The influence of the translational partition function of the activated complex is negligible in the kinetics and this means that $F_{H^*D^*,i}/F_{H^*D^*,o} = 1$. (ii) The interaction energy of the activated complex with its neighbourhood is attractive. (iii) The lateral interaction for NN and NNN for H and D must be of the same value but different signs. (iv) The H and D atoms have the same heterogeneity in the type-III sites, and these interactions are attractive. The existence of the heterogeneity allows us to explain the great change with the coverage in the pre-exponential factor that has been found experimentally. (v) The reconstruction parameters λ for H and D must be the same. Condition (iii) does not have much theoretical support. We suspect that the inconsistency is related to the fact that experimental data [3] were processed using an isotherm equation valid for an ideal adsorbate.

References

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